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# Speciation of Selenium in Groundwater

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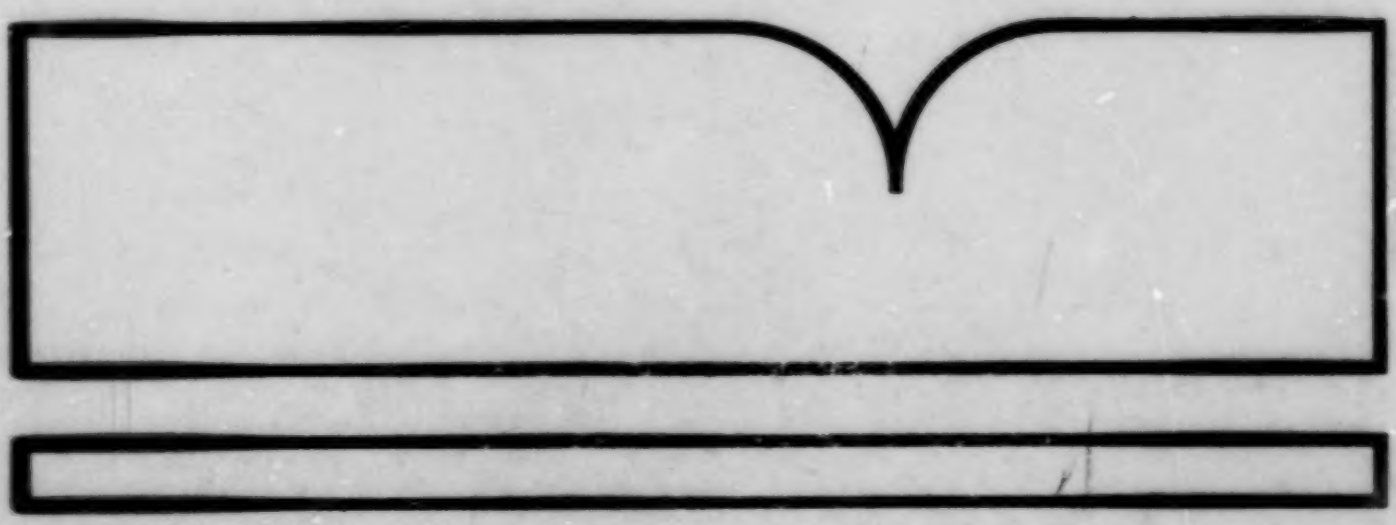

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# SPECIATION OF SELENIUM IN GROUNDWATER

by

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16. ABSTRACT

A study was conducted to investigate ion chromatography (IC) for determining selenium species in groundwaters. Analytical speciation of selenium was investigated because the removal efficiencies of various processes for selenium removal (activated alumina in particular) depend on which species (Se IV or Se VI) is predominant in the groundwaters.

In addition to investigating IC, the study aimed to determine a preservation technique for maintaining species integrity, and to analyze field samples taken from seleniferous regions to assess which of the two selenium species predominates.

Results showed the IC is suitable for selenium (VI) analysis in groundwater samples if the sample is pretreated with a $Ba(OH)_2$ dose to remove the sulfate interference. The selenium (IV) concentration can then be determined as the difference between the total selenium concentration (as determined by furnace atomic absorption spectroscopy), and the selenium (VI) value as determined by IC. The detection limit for selenium (VI) in groundwater samples treated with $Ba(OH)_2$ is approximately 0.020 mg/L. IC should therefore determine the predominant selenium species in a groundwater if the total selenium concentration is above 0.050 mg/L.

The analysis of field samples did not conclusively determine the predominant selenium species because only 30% of the collected samples had total selenium values above 0.050 mg/L. Neither species predominated in the samples that were analyzed.

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## FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution, and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and is a most vital communications link between the researcher and the user community.

Groundwater supplies located in seleniferous areas of the country frequently exceed the EPA Maximum Contaminant Level (MCL) of 0.01 mg/L and the effectiveness of removal methodologies are dependent on the selenium species present. This report evaluates ion chromatography as a potential analytical tool for determining selenium species in drinking water sources.

Francis T. Mayo, Director
Municipal Environmental Research
Laboratory

## ABSTRACT

A study was conducted to investigate ion chromatography (IC) for determining selenium species in groundwaters. Analytical speciation of selenium was investigated because the removal efficiencies of various processes for selenium removal (activated alumina in particular) depend on which species (SeIV or SeVI) is predominant in the groundwaters.

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This report was submitted in fulfillment of Contract No. C2282NAST by J. M. Montgomery, Consulting Engs., Inc. under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period 3/15/82 to 3/15/83, and work was completed as of 6/15/84.

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## List of Abbreviations and Symbols

Abbreviations

| | |
|---|---|
| AAS | atomic absorption spectroscopy |
| CO | Colorado |
| DI | deionized |
| gm/L | grams per liter |
| IC | ion chromatography |
| KS | Kansas |
| MCL | Maximum Contaminant Level |
| ug/L | microgram per liter |
| ul | micro liter |
| umho | micro mho |
| uS/ppb | microsiemen per part per billion |
| meqv/gm | milliequivalent per gram |
| mg/L | milligram per liter |
| ml/min | milliliter per minute |
| mm | millimolar |
| mV | millivolt |
| m | molar |
| OK | Oklahoma |
| ppb | part per billion |
| SD | South Dakota |

Symbols

| | |
|---|---|
| Ksp | solubility constant |
| pK | negative logarithm of the acidity constant |
| $\sigma$ | standard deviation |

## SECTION 1

## INTRODUCTION

The total selenium concentration in potable water is Federally regulated not to exceed 0.010 mg/L because of potential health effects[1]. Many groundwater supplies in seleniferous areas of the country such as South Dakota, Colorado, Oklahoma, Kansas, Wyoming, and southern California contain selenium levels considerably above the Federal limit. An effective removal technology is required if these drinking water supplies are to meet the standard.

Activated alumina was investigated as a selenium removal technique in earlier studies sponsored by EPA[2], but its removal efficiency depends on the selenium species present. Alumina effectively removed selenium in the +IV valence state (selenite) but not in the +VI valence state (selenate). The difference is due to the lower absorption affinity of Se (VI) and its greater susceptibility to interferences from other anions. Earlier investigations[3] of other treatment processes, including coagulation with alum or ferric sulfate, revealed the same poor removal of Se (VI). Ion exchange preferentially removes sulfate over Se (IV) and removes sulfate and Se (VI) equally. Reverse osmosis is effective for removing both species of selenium but the operational cost is too high for routine applications.

The predominant selenium species in ground water supplies is not well characterized because the element is regulated as total selenium, and the EPA-approved analysis method is atomic absorption spectroscopy (AAS), which cannot differentiate between species. Determination of the predominant selenium species in groundwater supplies containing significant amounts of selenium is needed to assess the feasibility of selenium removal by activated alumina.

There is a vast range of documented methodologies for determining Se(IV) such as fluorometry[4], electron-capture gas chromatography[5], hydride generation AAS[6], and x-ray fluorescence[7], but none of the procedures are straightforward. All require organic solvent extractions or preconcentration schemes to lower the detection limit[4]. Furthermore, none of these methods is capable of direct determination of Se(VI) which can only be determined by difference between Se(IV) and total selenium concentrations. The technique of ion chromatography is rapid and simple, requires no sample pretreatment that could alter speciation, and has the capability of detecting both selenium species simultaneously. Refinement of the method is required, however, to achieve adequate sensitivity to detect selenium species at the ug/l level and to elimnate interferences from other anions.

This study evaluates Ion Chromatography (IC) as an analytical method for determining selenium species in groundwaters. Optimization of instrumental sensitivity and selectivity for the selenium species was investigated by varying instrumental parameters and, if required, establishing initial pretreatment schemes to eliminate interferences. Sample preservation techniques were also investigated to develop a scheme that would preserve the integrity of the selenium species. Finally, selected groundwater samples from seleniferous regions were analyzed to determine which selenium species, if any, predominates in the environment.

## SECTION 2

## CONCLUSIONS

IC is an accurate, rapid method for selenite and selenate analysis when the concentrations of sulfate, chloride, and nitrate are low enough not to interfere. Variation of instrumental parameters was ineffective in mitigating these interferences. In typical groundwaters, the levels of these interfering anions are too high to allow detection of selenite or selenate by IC without chemical pretreatment. Addition of $Ba(OH)_2$ successfully removes the sulfate interference without loss of selenate when the barium dose is stoichiometrically matched to the sulfate concentration. The increase in sample pH resulting from the addition of the barium as hydroxide does not appear to alter the speciation. Addition of ion-exchange resin in the silver form should remove the interference of chloride with selenite but was not investigated in this study.

The instrumental detection limit for either species in deionized water is 8 ug/L. Use of offline loading of a concentrator column might improve the detection limits, but it would also increase the concentration of interfering anions. The selenate detection limit in groundwater samples treated with $Ba(OH)_2$ is approximately 15 to 25 ug/L. With $Ba(OH)_2$ pretreatment, IC should determine the predominant species in a groundwater sample if the total selenium concentration is at least 50 ug/L.

Analysis of 21 groundwater samples collected from Kansas, Colorado, Oklahoma, and South Dakota revealed that only eight of the samples (38%) had total selenium values above 30 ug/L. Three of the 8 samples were not analyzed because one of them had already been dosed with chlorine which could alter speciation and the other 2 exceeded the established holding period. The five remaining samples were analyzed by IC and three had detectable selenate values. Selenite was detected in only one of the 5 analyzed samples because the chloride and nitrate concentrations were too high in the other samples to permit resolution of the selenite peak. The sum of the selenite and selenate values for this sample was in excellent agreement with the total selenium value determined by graphite furnace AAS. For the 3 samples having detectable selenate values, the distribution of species was 50% selenite/50% selenate in two of the samples, and 70% selenite/30% selenate in the third.

A preservation study of mixed selenite-selenate DI water standards revealed no species deterioration or conversion over a 3-week period for a variety of preservatives, bottle materials and sizes, and storage temperatures. The only preservative that interfered with species integrity was additon of 0.1 ml of concentrated nitric acid to 500 ml of sample (3.2 mM). Immediately after its addition, all the selenate converted to selenite. Two of the field samples were re-analyzed after an 8-week holding period, and the results were compared with the 4-week analysis. Significant decreases (50% and 70%) in the total selenium values had occurred in both the unpreserved and acid preserved aliquots analyzed by graphite furnace AAS. Analysis of one of these samples by IC revealed that the selenite had decreased by 70% and the selenate had increased by 40% of their original values. Holding time therefore appears to be critical in obtaining accurate values for selenium species and total selenium.

This study was inconclusive in evaluating the predominant selenium species in groundwaters from seleniferous regions because of the low levels of total selenium present in most of the collected samples.

## SECTION 3

## RECOMMENDATIONS

Field samples should be collected from sources with documented high levels of total selenium (greater than 50 ug/L) and analyzed by IC after $Ba(OH)_2$ pretreatment to ascertain the predominant selenium species.

Three analytical options to improve instrumental detection limits for selenite and selenate or mitigate interferences could be evalutated. These options are use of off-column loading, use of IC for species separation with detection by graphite furnace AAS, recycle ion chromatography, and use of ultraviolet (UV) detection IC in place of conductivity detection IC. The first two methods would improve detection limits at the expense of increased interferences, and the fourth would remove interferences at the expense of instrumental sensitivity. Experimental work is needed to see if any of these options are an improvement over the methodology developed in this study.

## SECTION 4

## SELENIUM SPECIATION

Inorganic selenium is found in the environment with an oxidation state of -2,0,+4, or +6. Construction of an Eh-pH diagram from the appropriate redox and acid-base reactions provides a theoretical indication of which species might predominate under a given set of environmental conditions. The Eh-pH diagram for selenium is shown in Figure 1 with the normal Eh-pH range of water indicated as the area contained within the two dotted boundary lines.[5] Based on the figure, the only soluble inorganic selenium species expected in ground waters will be either Se(VI) or Se (IV). Se(VI) will occur as $SeO_4^{=}$ because selenic acid ($H_2SeO_4$) is an extremely strong acid (pK=-3) and the protonated form ($HSeO_4^-$) does not occur above pH 4. Selenious acid ($H_2SeO_3$) is a much weaker acid (pk=2.7), and Se(IV) will occur predominately as the monoprotic species ($HSeO_3^-$) in the 6-9 pH range typical of most ground waters. Attempts to make further use of the diagram to predict whether Se(IV) or Se(VI) dominates a particular groundwater based on its anoxic character is questionable. The diagram is derived from thermodynamic equilibria and does not take into account the influence of kinetics and biological mediation in stabilizing thermodynamically unstable species. Furthermore, selenite has a much lower solubility than selenate, and will be more freely scavenged by particulates, thereby lowering its concentration.

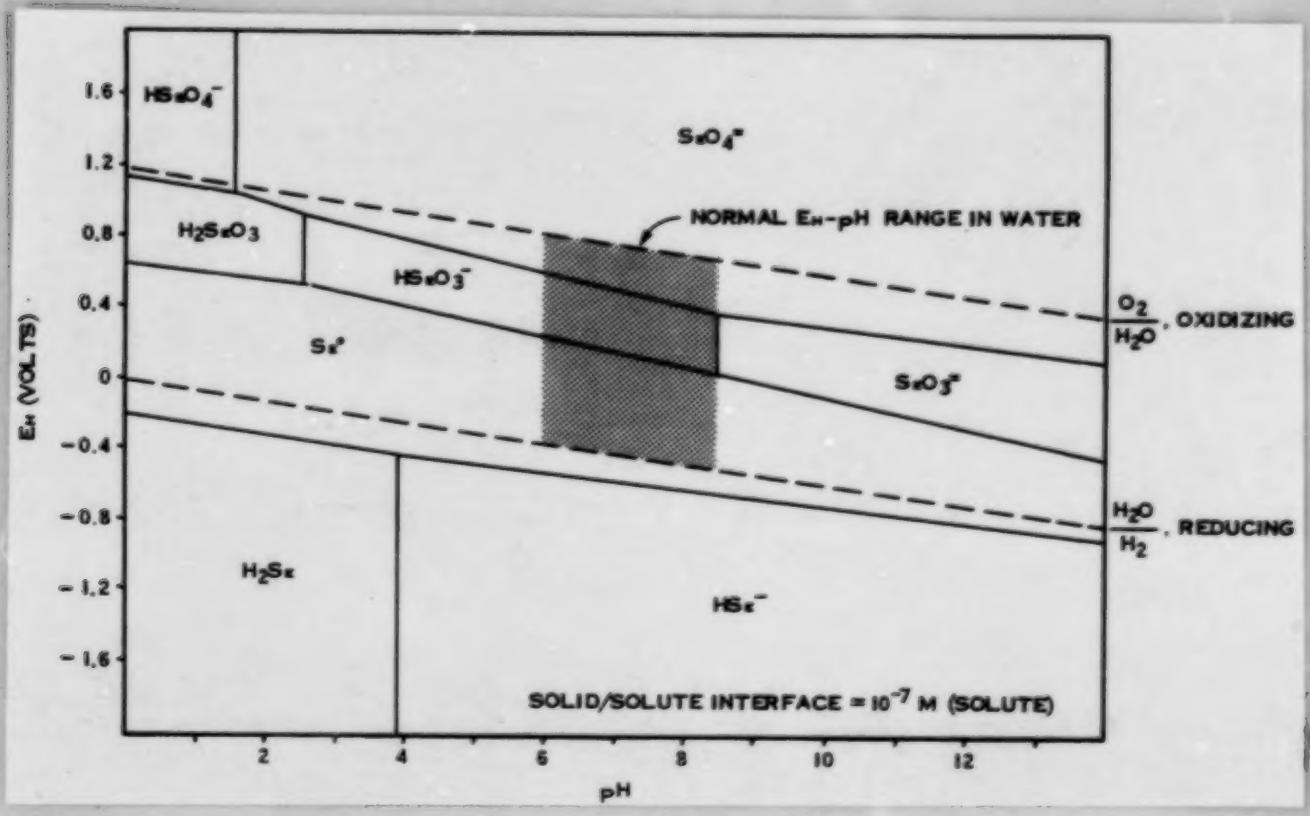



**FIGURE 1. Eh-pH DIAGRAM FOR SELENIUM [8]**

## SECTION 5

## INSTRUMENTATION

### THEORY

Ion chromatography (IC) is a form of liquid chromatography. Conventional suppressed IC consists of a low capacity pellicular ion-exchange resin separator column coupled to a high capacity ion-exchange resin suppressor column and a conductivity detector. When the instrument is configured for anion analysis, the separator column consists of fully aminated active anion exchange sites. The volume of sample loaded into the instrument is controlled by the size of a sample loop. Upon injection, the sample is carried through the separator column by an eluent stream which, for anion analysis, is typically .003 M NaHC03/.0024 M Na2C03.

The period of time a particular anion is retained on the resin is a function of its valence, ionic charge, and Van der Waals effects. After species separation is achieved by the separator column, the eluent stream carries the anions through the suppressor column which contains sulfonated cation exchange sites. The anions of interest are converted to their more conductive acid analogs while the HC03-/CO3= eluent is converted to less conductive H2C03. Adequate sensitivity by conductivity detection is now possible since the background conductivity has been suppressed and the anion conductivities have been enhanced. Anions are identified according to peak retention times, and quantification is based on peak heights or areas. A flow scheme depicting the process of anion separation and detection is given in Figure 2.[6]

### INSTRUMENTAL PARAMETERS AFFECTING RESOLUTION

Peak resolution is a function of the separator column's efficiency, capacity, and selectivity. A brief description follows for each of these column characteristics and how they can be varied by changing instrumental parameters.

#### 1a. Column Efficiency

Column efficiency equates to the number of theoretical plates contained in the column. A theoretical plate is an imaginary construction representing a thickness of column layer at which the eluent would have the composition it would achieve if equilibrium existed between the mobile and immobile phases midway in the layer. Efficiency is dependent on the peak width relative to its retention time. Decreasing the eluent flow rate or increasing the column length will increase retention times which increases column efficiency but this is achieved at the expense of increased band broadening which decreases column efficiency.

#### 1b. Column Capacity

Column capacity is a measure of the number of exchange sites per unit volume or unit weight of resin and therefore relates to the rate at which a particular species travels through the column. Capacity for a given species may be defined empirically as the ratio of the retention volume (or time) to the unretained "void" volume (or time). This ratio is referred to as the partition coefficient. Only low capacity resins on the order of 0.02 meq/gm are utilized in ion chromatography.

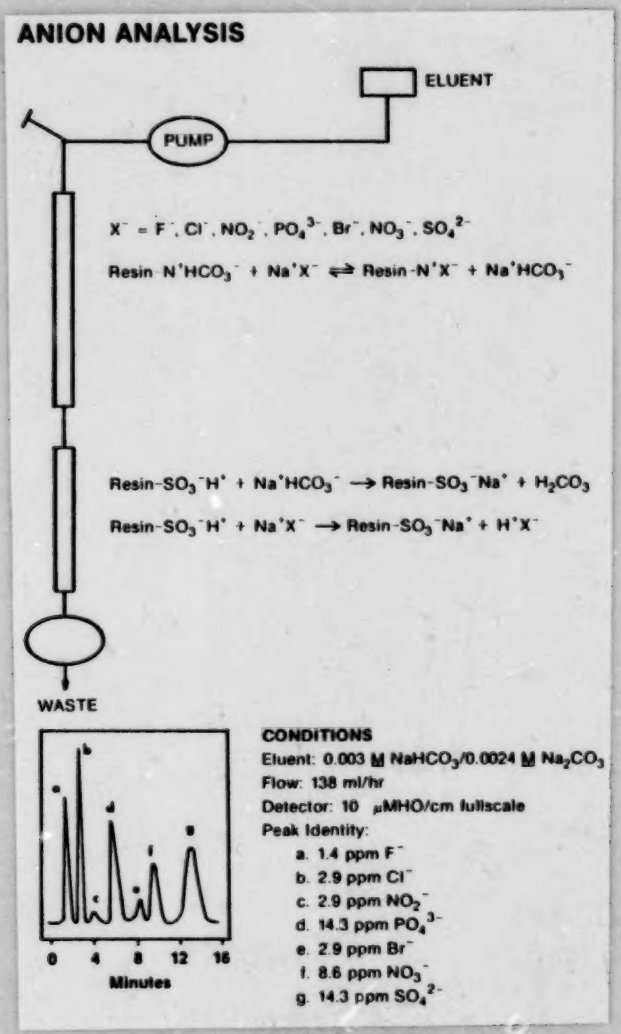



**FIGURE 2. FLOW SCHEME FOR ANION ANALYSIS BY IC[9]**

(Reprinted with permission of the Dionex Corp.)

Column capacity is controlled mainly by the resin columns Dionex chooses to market. For any given column, the capacity can be increased by using a weaker eluent or increasing the effective length of a column by placing 2 columns in series. Dionex offers 3 different separator columns for use on the Model 16. A newer, fourth column is available only for the Model 2000 Series. The AS1 column has more capacity than the "fast run" AS3 column. Under standard operating conditions, sulfate elutes in 18 minutes using an AS1 column, and in only 7 minutes with the AS3. The AS2 column reverses the standard elution order of nitrate and sulfate because this resin has a different selectivity from the other 2 columns.

### 1c. Column Selectivity

Column selectivity measures the relative speed at which two different species travel through the column. Since speed of passage through a column is a function of a species partition coefficient, the selectivity is obtained from the ratio of the coefficients for the two species. Factors which increase a species partition coefficient or retention on the column are its valence, ionic size, and the influence of Van der Waals forces.

Column selectivity can be modified by changing the stationary phase as occurs when an AS2 column is used in place of an AS1. Selectivity can also be altered by changing to a different eluent or eluent strength, since the new eluent could affect a species valence or ionic size. As an example, weakening the HC03-/C03= eluent by increasing the ratio of bicarbonate to carbonate concentrations will lower the eluent's pH and could decrease the valence of selenite or selenate ions due to protonation. This would result in a decrease in the resin's selectivity for these species and they would elute earlier. Examination of the Eh-pH diagram for selenium indicates that eluent modification might affect the retention time of selenite but would probably not influence the retention time of selenate due to its small pK.

## SECTION 6

## EXPERIMENTAL PROCEDURES

### INSTRUMENTATION

The IC used in this study was a Dionex Model 16 with conductivity detection. Hardcopy output was collected on a Pederson recorder and peak quantification was performed manually by measuring peak heights. Manual measurement of peak heights was performed rather than computerized peak integrations because of the difficulty in setting adequate integration baselines for poorly resolved peaks. Table 1 lists the standard instrumental operating conditions and columns that were used.

Selenite and selenate standards of 25 and 50 ug/L were analyzed by IC under standard operating conditions to determine retention times and sensitivities. A mixed 25 ug/L selenite, 25 ug/L selenate standard was made up fresh each analysis day and run by IC to determine any significant change in peak height for either species. The peak height values obtained for the selenite and selenate standards over the duration of the project were recorded.

Due to slight instrument variations, the peak heights for the selenite and selenate changed slightly from day to day. Evidence of contamination or degeneration of a stock would appear as a steadily increasing or decreasing peak height value more than 2 $\sigma$ away from the mean. No such evidence was observed during the duration of the project.

### REAGENTS

#### 10 mg/L Selenite and 10 mg/L Selenate Stocks

Separate stock solutions of 10 mg/L selenite and 10 mg/L selenate were prepared from Ventron Corp., Alfa Products reagent grade sodium selenite (Na2Se03) and sodium selenate (Na2Se04). The stock concentrations were initially verified by graphite furnace AAS.

#### 100 mM Barium Hydroxide Stock

A 100 mM barium hydroxide stock was prepared for spiking field samples to remove interfering sulfate. The concentration of the stock was initially verified by inductively coupled plasma emission spectroscopy. The stock had a tendency to precipitate over time and therefore, the calculated spikes for samples were usually too low to eliminate the sulfate interference and had to be repeated with larger spikes. Use of a lower stock concentration to prevent precipitation was not considered because the spike volumes would have been too large.

### PRESERVATIVES

Cadmium metal was added to a 500 ml selenite-selenate standard as a piece of reagent-grade mossy cadmium metal.

Thiosulfate was added to a 500 ml selenite-selenate standard as 4 drops of saturated solution.

Perchloric Acid was added to a 500 ml selenite-selenate standard as 1 ml of 70% reagent-grade perchloric acid.

Nitric acid was added to a 500 ml selenite-selenate standard as 0.1 ml of concentrated reagent-grade nitric acid.

Formaldehyde was added to a 500 ml selenite-selenate standard spiked with bacteria as 0.5 ml of 37% formalin.

**TABLE 1. STANDARD INSTRUMENTAL OPERATING CONDITIONS**

| | |
|---|---|
| Columns: | 4x5 mm Fast-Run (AS3) Pre-Column (P/N 030831)<br>4x250 mm Fast-Run (AS3) Separator Column (P/N 030831)<br>Fiber Suppressor Column (P/N 35350) |
| Eluent: | 0.003 M $NaHCO_3$/0.0024 M $Na_2CO_3$ |
| Eluent Flow Rate: | 2.07 ml/min |
| Sample Loop Size: | 600 ul |
| Detector Sensitivity: | 0.3 umho/full scale |
| Recorder Sensitivity: | 100 mV/full scale |

## SECTION 7

## RESOLUTION RESULTS

### RETENTION TIMES, SENSITIVITIES, AND DETECTION LIMITS

Twenty-five and 50 ug/L selenite and selenate standards made up from stocks diluted with deionized water were analyzed by IC under standard operating conditions to determine retention times and sensitivities. Retention times, instrumental sensitivities, and detection limits for selenite, selenate, and some of the common anions which should be present in ground waters at significant levels are presented in Table 2. The selenite and selenate detection limits of 8 ug/L are only marginally acceptable in light of EPA's current maximum contaminant level (MCL) of 0.01 mg/L for total selenium. However, research such as this could lead to lower detection limits for selenium species.

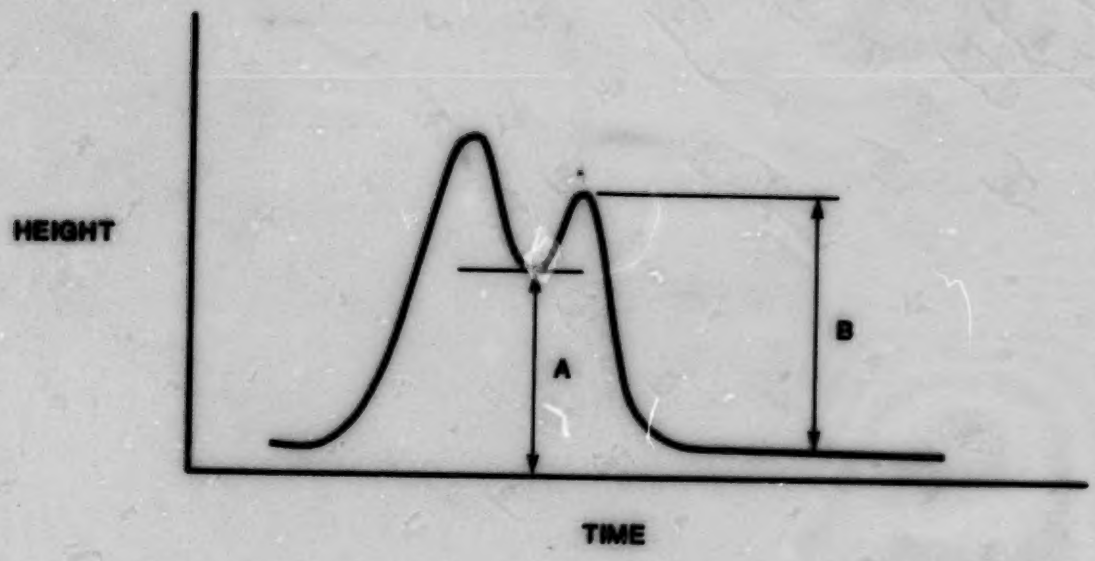
### INTERFERENCES

The retention time of sulfate is close enough to the retention time of selenate that a sulfate concentration of sufficiently large magnitude compared to the selenate concentration could swamp out the selenate peak. In groundwaters containing selenium levels above the maximum allowable concentration of 0.01 mg/L the sulfate concentration is typically 3 orders of magnitude higher with levels ranging from 100-1000 mg/L. This indicates a probable interference problem between the selenate and sulfate peaks. A similar interference potential exists between low levels of selenite and the much higher chloride and nitrate concentrations anticipated in groundwaters because the selenite peak is sandwiched between the chloride and nitrate peaks.

To discern the magnitude of this potential interference, mixed selenate-sulfate standards and mixed selenite-chloride standards were run by IC. The degree of resolution between peaks was quantified as the practical percentage resolution which is defined in Figure 3. A standard solution of 10 ug/L selenate and 100 mg/L sulfate gave no resolvable selenate peak at the most sensitive detector setting. A 50 ug/L selenate, 100 mg/L sulfate standard gave no practical resolution, but the selenate could be detected as a flat-topped peak on the shoulder of the sulfate peak as shown in Figure 4. This degree of resolution allows for detection of selenate, but quantification is not possible. Likewise, 50 ug/L selenite in the presence of 100 ug/L chloride gave no discernable selenite peak. These results imply that standard instrumental settings will not be adequate for achieving sufficient resolution in natural groundwater samples where the chloride and sulfate values are expected to be around 3 orders of magnitude higher than the selenium species concentrations.

### MODIFYING INSTRUMENTAL PARAMETERS

Variations of the instrumental parameters discussed in Section 5 were investigated as a means of achieving adequate resolution between the selenate and sulfate peaks.




PRACTICAL % RESOLUTION = 100(1 - A/B)

FIGURE 3. DEFINITION OF PRACTICAL % RESOLUTION

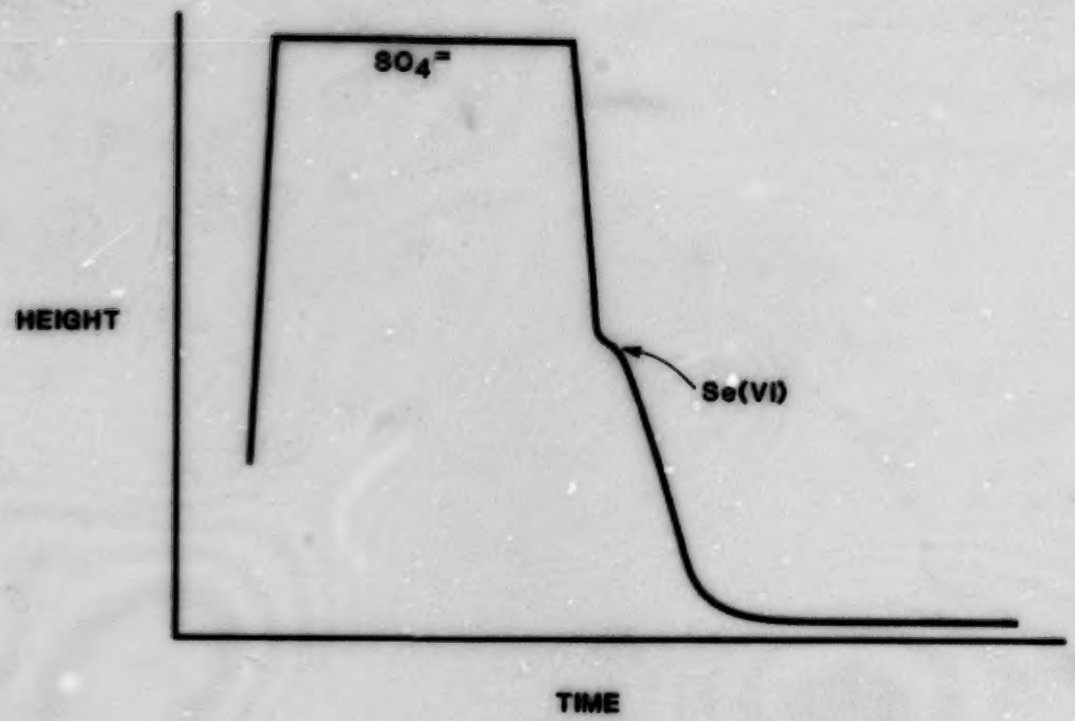



FIGURE 4. ILLUSTRATION OF THE POOR RESOLUTION BETWEEN 50 PPB SELENATE AND 100 PPM SULFATE

**a) Column Efficiency**

Column efficiency was increased by reducing the eluent flow rate from 2.1 ml/min to 1.3 ml/min. Even at the lower eluent flow rate, the selenate peak remained completely unresolved from the extremely large sulfate peak.

**b) Column Capacity**

Two AS3 separator columns were connected in series to study the effect of increasing column capacity on the resolution of the selenate and sulfate peaks. Use of these 2 columns in series increased the retention time of selenate from 11.8 minutes to 24 minutes. A 50 ug/L selenate, 100 mg/L sulfate standard still showed 0% practical resolution, with the selenate present only as a flat-topped peak on the shoulder of the sulfate peak as had occurred for these concentrations using a single separator column. This degree of resolution allows for detection of selenate, but quantification is not possible. A 100 ug/L selenate, 100 mg/L sulfate standard gave 35% practical resolution. Because resolution was still poor with two AS3 columns in series, use of a single AS1 column in place of the AS3 column or use of a weaker eluent were not investigated as viable solutions to the resolution problem.

**c) Column Sensitivity**

Selenate elutes shortly after sulfate because both species have identical valences but selenate has a slightly larger covalent radius. Switching from an AS3 separator column to an AS2 column changes column sensitivity. Use of this column was not investigated because it changes the elution order of the nitrate peak but doesn't change the elution order of selenate and sulfate. Use of a weaker HC03-/C03= eluent would not decrease selenate's retention time because selenate is the conjugate base of selenic acid which has a pk of -3. Therefore, there is no way to alter column selectivity such that the resolution between selenate and sulfate can be improved.

**TABLE 2. RETENTION TIMES, SENSITIVITIES, AND DETECTION LIMITS FOR SELENITE, SELENATE, AND OTHER COMMON ANIONS**

| ANION | RETENTION TIME (Minutes) | SENSITIVITY (uS/ppb) | DETECTION LIMIT (ppb) |
|---|---|---|---|
| Selenite | 4.6 | .0013 | 8 |
| Selenate | 11.8 | .0013 | 8 |
| Chloride | 2.4 | .012 | 1 |
| Nitrate | 6.6 | .012 | 1 |
| Sulfate | 8.4 | .002 | 5 |

## CHEMICAL PRETREATMENT

Since adequate resolution between the selenate and sulfate peaks was not achieved by varying instrumental parameters, the next step was investigation of chemical pretreatment to eliminate the sulfate interference. Addition of a barium salt to a selenate-sulfate standard was investigated as a means of eliminating the sulfate interference through its precipitation as barium sulfate. This form of pretreatment should remove the sulfate without precipitating any selenate because the solubility product of $BaSO_4$ is approximately three orders of magnitude lower than that of $BaSeO_4$ and the selenate concentration in ground waters is typically three orders of magnitude lower than the sulfate concentration. The solubility products and solubilities for $BaSO_4$ and $BaSeO_4$ are given in Table 3. Based on calculations using these solubility products, a 500 ug/L selenate concentration would not begin to precipitate upon addition of barium until the added barium was 7 grams in excess of the quantity needed to stoichiometrically match the sulfate concentration in the sample. Although solubility calculations indicate that barium addition should not cause precipitation of selenate, there is still the possibility of selenate loss occurring with the precipitating $BaSO_4$ in a sweep floc effect. To empirically test the efficacy of barium addition, a set of selenate-sulfate standards were analyzed with and without the addition of barium.

### Stoichiometric Dosing

Initially, a 25 ug/L selenate, 100 mg/L sulfate standard was made up with approximately 1 mM barium present as $Ba(OH)_2$. The standard was loaded into the IC through a 0.45 micron filter which removed the precipitated barium sulfate. Addition of the barium salt to this standard increased the practical percentage resolution from 0 to 41% and did not result in any selenate loss. This preliminary result indicates that barium addition will effectively eliminate the sulfate interference and maintain the integrity of the selenate concentration when the quantity of added barium is stoichiometrically matched to the sulfate concentration.

### Non-Stoichiometric Dosing

Experiments were performed to discern the effectiveness of barium addition when the addition is not stoichiometrically matched to the sulfate concentration. If matching is not necessary, a sample of unknown composition could be analyzed for selenate simply by adding a 5 mM Ba dose. A 5 mM Ba dose would precipitate up to 500 mg/L of sulfate, which should be the maximum concentration of sulfate found in most ground waters. If stoichiometric matching proved to be necessary, a preliminary sulfate analysis would be required in order to calculate the barium dose prior to performing the selenate analysis. Elimination of the need to add a stoichiometrically matched barium dose would therefore result in a considerable savings of time and labor.

The experiment consisted of dosing three selenate standards containing different concentrations of sulfate with a 5 mM barium dose. Each standard contained 25 ug/L selenate and the sulfate concentrations were 0, 50, and 500 mg/L respectively. The results of the experiment are presented in Table 4.

TABLE 3. SOLUBILITY PRODUCTS AND SATURATION SOLUBILITIES FOR BARIUM SULFATE AND BARIUM SELENATE

| | SOLUBILITY PRODUCT (Ksp) | SATURATION SOLUBILITY (gm/L) |
|---|---|---|
| $BaSO_4$ | $1.1 \times 10^{-10}$ | 0.00233 |
| $BaSeO_4$ | $1.76 \times 10^{-7}$ | 0.118 |

TABLE 4. EXPERIMENTAL RESULTS OF 5 mM BARIUM ADDITION TO SELENATE-SULFATE STANDARDS

| | Before Dose | | | After Dose | | |
|---|---|---|---|---|---|---|
| Stnd# | $Se^{+6}$ Concentration (ug/l) | $SO_4^=$ Concentration (mg/l) | % Resolution (%) | $Se^{+6}$ Concentration (ug/l) | $SO_4^=$ Concentration (mg/l) | % Resolution (%) |
| 1 | 25 | 0 | — | 25 | 0 | — |
| 2 | 25 | 50 | 0 | 14 | 1 | 100 |
| 3 | 25 | 500 | 0 | * | 67 | < 5 (shoulder peak) |

*Difficult to quantify due to poor resolution of peak

No loss of selenium occurs upon addition of 5 mM barium when no sulfate is present. For the case of 5 mM barium addition to the 500 mg/L sulfate standard, the barium dose stoichiometrically matches the sulfate concentration. The results of the stoichiometric dosing were inconclusive because the selenate peak was poorly resolved from the residual sulfate peak remaining after dosing. Achieving an exact stoichiometric match between the barium and sulfate concentrations was difficult because the barium stock used for dosing had a tendency to precipitate. A lower concentration barium stock could not be used because the spike volumes would be too large and might affect the overall sample matrix. Although the results of stoichiometric dosing were inconclusive here, earlier stoichiometric barium dosing of a 25 ug/L selenate, 100 mg/L sulfate standard was successful in eliminating the sulfate interference while maintaining the selenate concentration. Addition of 5 mM barium to the standard containing 50 mg/L sulfate eliminated the sulfate peak interference but the selenate concentration decreased to half its original value. Apparently, selenate will be precipitated from solution if some sulfate is present and barium is added in excess of the sulfate concentration. The 50 mg/L sulfate standard was rerun with a reduced barium dose of 0.5 mM (stoichiometric) in order to determine if selenate precipitation would occur when the barium dose was stoichiometrically matched to the 50 mg/L sulfate present. Addition of 0.5 mM barium eliminated the sulfate interference and maintained the selenate concentration at its initial value of 25 ug/L.

The results of these barium dosing experiments seem to indicate that barium addition is an effective pretreatment scheme for eliminating interfering sulfate only if the barium dose is stoichiometrically matched to the sulfate concentration present in the sample. Therefore, to use barium dosing as a pretreatment scheme, the sulfate concentration of the sample must be determined first in order to calculate the appropriate barium dose to use prior to selenium analysis by IC.

**pH Effects of Barium Hydroxide Dosing**

Barium hydroxide was chosen for the barium dosing because it is one of the only barium compounds which is sufficiently soluble in water and does not introduce interfering anions to the sample as in the case of barium chloride or barium nitrate. Pre-treatment of a sample by addition of barium hydroxide will, however, substantially increase the pH of the sample and possibly alter the selenium speciation. Addition of 5 mM barium as barium hydroxide raises the pH of a mixed selenate-sulfate standard from 6 to 12. To investigate the effect of this pH change on speciation, 5 mM barium as barium hydroxide was added to a mixed 100 ug/l selenite, 100 ug/l selenate standard. An ion chromatographic scan of this standard before and after the barium addition indicated that no shift in speciation had occurred due to the increased pH.

Although the pH increase due to addition of barium hydroxide does not appear to alter the selenium speciation in a mixed standard, it might influence speciation in the complex matrix of a real sample. To eliminate changing the sample pH upon addition of barium, conversion of the ion-exchange resin to the barium form was investigated. Use of resin would enable barium to be added to a sample without the concurrent introduction of interfering anions or hydroxide ions which would alter the sample pH. Bio-Rad 50-100 mesh cation exchange resin was converted to the barium form and added to a standard containing 25 ug/l selenite, 25 ug/l selenate and 500 mg/l sulfate. Addition of the resin did not induce precipitation of the sulfate probably because there was an insufficient concentration of cations in the sample to exchange with the strongly held barium ions.

The results of the chemical pretreatment studies indicate that stoichiometric addition of $Ba(OH)_2$ is the most viable method for eliminating sulfate interference in ground water samples being analyzed for selenate by IC. The scope of this study did not allow for a similar detailed investigation of the chloride-selenite interference problem. Since this interference is similar to the selenate-sulfate interference, variation of instrumental parameters would probably not achieve adequate resolution. It is common practice in ion chromatographic analysis, to remove chloride interference by pretreating the sample with ion-exchange resin in the silver form. Since silver is not strongly retained by the resin, an adequate supply is available to precipitate the chloride interferent. Insufficient time was available to investigate the removal of chloride by addition of silver resin and this report concentrates on optimizing detection of selenate and obtaining selenite as the difference between the total selenium and selenate concentrations.

## SECTION 8

## PRESERVATION STUDY

The EPA-approved methodology for preserving samples for total selenium analysis consists of sample collection in polyethylene bottles and acidification with nitric acid to a pH less than 2. The optimal preservation technique for selenate and selenite species is not as clear, since addition of acid could cause species conversion. Nitric acid addition could also interfere with selenate analysis by ion chromatography because the introduction of the 630 mg/l of nitric acid (10 mM) needed to reduce the sample pH to 2 would result in a nitrate peak which might overshadow the selenate peak. Numerous studies on the stability of selenium species in aqueous samples and methods of preservation to insure speciation integrity can be found in the literature. The variables considered in this type of study are the size and material of the storage container, the type of water matrix studied, the concentration level of selenite or selenate spiked into the water sample, the type of chemical preservative added, the temperature maintained during storage, and the duration of the monitoring period. In reviewing some of the published studies, it became apparent that many of the results are contradictory making it impossible to discern an optimum preservation method.

### LITERATURE REVIEW

Massee[10] reported no loss of selenite at the 8 ug/l level in DI and artificial seawater when stored in borosilicate glass, polyethylene, or teflon. Shendrikar and West,[11] on the other hand, observed losses of selenite in aqueous solutions ranging from 4-8% in these type of containers after 15 days. Of course, Shendrikar's selenite concentration of 1 mg/l was much higher than Massee's 8 ug/l and provides an indication as to why conclusive results cannot be drawn from the various preservation studies.[4] With so many variables to control, it is almost impossible to find two separate studies that have duplicated one another and reached identical conclusions.[5] Many studies, such as Shendrikar's, have also been criticized for using unrealistically high selenium species concentrations which do not model the ug/l levels found in the environment.

Similar contradictory findings can also be cited for selenate. Cheam and Agemian[12] observed no loss of selenate from DI water stored in various bottle types at three different pH's while Cutter[13] observed selenate loss of approximately 50% occurring in less than 7 days in unacidified samples stored in Pyrex or polyethylene. Since Cutter does not indicate the selenate concentration used in his work, it is difficult to resolve the descrepancies between these studies. They may be due to a different selenate concentration, some difference in the water matrices used, or some other anomaly.

### EXPERIMENTAL STUDY

In light of the confusion surrounding preservation techniques for maintaining selenium speciation integrity, a preservation study was run to discern an adequate preservation method which would not interfere with the ion chromatographic analysis. Mixed 25 ug/l selenite and 25 ug/l selenate DI water standards were stored with various preservatives and in different types of containers. A concentration of 25 ug/l was chosen because the instrumental detection limit of 8 ug/l would make it difficult to observe a concentration decrease if a lower starting concentration was used. The container types, container sizes, and

preservatives that were evaluated are listed in Table 5. The selenite and selenate concentrations were monitored approximately every 4 days over a 3-week period.

**TABLE 5. PRESERVATION METHODS EVALUATED TO MAINTAIN SELENIUM SPECIATION INTEGRITY**

A. 500 ml polyethylene - Freeze

B. 500 ml polyethylene - Refrigerate

C. 125 ml polyethylene - Refrigerate

D. 500 ml amber glass - Refrigerate

E. 125 ml amber glass - Refrigerate

F. 500 ml amber glass - Cd Metal Reducing Agent, Refrigerate

G. 500 ml amber glass - Thiosulfate Reducing Agent, Refrigerate

H. 500 ml amber glass - Perchloric Acid pH Reduction, Refrigerate

I. 500 ml polyethylene - Nitric Acid pH Reduction, Refrigerate

J. 500 ml amber glass - Formaldehyde Biological Inhibitor, Refrigerate

K. 500 ml polyethylene - Formaldehyde Biological Inhibitor, Refrigerate

L. 500 ml amber glass - Room Temperature Control

M. 500 ml polyethylene - Room Temperature Control

Two different bottle sizes were evaluated to determine whether an increased surface to volume ratio would lead to a noticeable increase in selenite or selenate adsorption. Only two bottle materials, glass and polyethylene, were evaluated in order to keep the total number of samples at a reasonable size and also because the literature did not reveal strong differences between different container types. All samples were refrigerated except for the glass and polyethylene room temperature controls and one other sample which was frozen.

The chemical preservatives evaluated fell into three categories: reducing agents, pH reducers, and biological inhibitors. Reducing agents were tried to see if they would prevent oxidation of selenite to selenate since ground water samples originate from an environment much more anoxic than the one they are stored in. Cadmium metal and thiosulfate were selected because cadmium will not give an interfering peak on an anionic chromatograph and thiosulfate has a large retention time and should elute well after the selenate peak. pH reduction was evaluated because it is the standard preservation technique for total selenium but pH reduction could cause species conversion. Nitric acid was chosen because it is the EPA recommended presentative for metals but the nitrate peak could interfere with the selenate peak. Perchloric acid was chosen because it is also a strong acid but its conjugate base (perchlorate) elutes much earlier than nitrate and might interfere less with the selenate peak. A biological inhibitor was investigated to determine whether bacterial activity in a field sample could be removing selenite or selenate. Since selenite and selenate spiked DI water was used for the preservation study,

the samples receiving the formaldehyde were first spiked with a bacterial population of approximately 1 x 103/ml. A control sample containing the bacteria without the formaldehyde was run simultaneously.

Perchloric acid addition was eliminated at the onset of the study because the perchlorate peak overshadowed both the selenate and the selenite peaks. Nitric acid addition had to be limited to 200 mg/l in order to prevent the nitrate peak from overshadowing the selenate peak. This quantity of acid reduced the pH of the sample to 2.5 which is slightly higher than the EPA recommended pH of $< 2$.

The integrity of the mixed selenite, selenate standards was maintained over the three week period for all of the preservation conditions except the nitric acid addition. Analysis of this sample immediately after addition of the acid revealed that all of the selenate had converted to selenite. Examination of the Eh-pH diagram in Figure 1 indicates that conversion of selenate to selenite could occur due to a drop in pH. Further evidence of this was reported by Cutter , who observed species conversion of 60% of selenate to selenite in a 4 mM HCl solution after 7 days. This conversion was not observed by Cutter in 1 mM HCl but, he may have been using much higher selenium concentration levels in his study.

Since all of the preservation methods appeared comparable in preventing loss or conversion of the selenite and selenate with the exception of acid addition, the field samples were collected in polyethylene cubitainers without added preservative. The field samples were refrigerated upon arrival until they could be analyzed.

## SECTION 9

## FIELD SAMPLE DATA

Selection of appropriate sites for collection of field samples was arranged by the EPA Project Officer. Water utilities located in suspected seleniferous regions in Kansas, South Dakota, Colorado, and Oklahoma were asked to submit groundwater samples for analysis. Upon receipt of a sample, an aliquot was transferred to a 60 ml polyethylene bottle and acidified to a pH $< 2$ with nitric acid for total selenium analysis by graphite furnace AAS. The remainder of the sample was refrigerated until it could be analyzed for pH alkalinity, sulfate, chloride, selenite, and selenate. The analytical methods used for each parameter are listed in Table 6. A total of 21 samples were received for analysis.

Sulfate concentrations of the samples were obtained in order to estimate the proper barium dose for the selenate analysis and also to determine whether there is any relationship between the selenate and sulfate concentrations in groundwaters. Chloride concentrations were obtained to assess the severity of the chloride-selenite interference problem. Alkalinity and pH were also analyzed in order to more fully characterize the different groundwater samples and determine whether higher concentrations of selenium occur in certain types of water.

The analytical results for the 21 field samples are given in Table 7. The total selenium concentrations in these samples ragned from 620 ug/l to $<1$ ug/l but 60% of the samples had values below 20 ug/l and 70% had values below 50 ug/l. Only one of the samples that had a total selenium value less than 20 ug/l was analyzed by ion chromatography for selenite and selenate because the instrumental detection limit for each species is 8 ug/l and therefore the matrix dependent detection limit is probably closer to 20 ug/l. This was sample G(KS), which had a total selenium concentration of 16 ug/l. As expected, neither selenite or selenate was detected in this sample.

Only 8 of the 21 samples had total selenium concentrations high enough to be detected by ion chromatographic analysis. Of these 8, sample U(SD) was not analyzed because the sample was collected after chlorination which might have altered the speciation by oxidizing selenite to selenate. Two others samples, P(CO) and S(OK) were not analyzed because they had been held too long before they could be analyzed.

Of the 5 remaining samples, one gave a detectable peak for selenite as well as selenate (A(KS)) because the chloride and nitrate concentrations were low enough to permit resolution of the selenite. The summation of the selenite and selenate concentrations obtained for this sample by ion chromatography (141 ug/l) is in excellent agreement with the total selenium value of 150 ug/l obtained by graphite furnace AAS, providing indirect verification for the accuracy of the IC results. Selenate was also detected in the B(KS) and I(CO) samples but the selenite was masked by interferences from the chloride and nitrate peaks. Quantification of the selenite in either of these samples was therefore only possible by difference between the total selenium concentration and the selenate concentration. Neither selenite or selenate could be detected in samples C(KS) or D(KS) which indicates that the selenate was probably present at a concentration below the matrix detection limit and the selenite was probably masked by nitrate and chloride interference.

## TABLE 6. ANALYTICAL METHODS USED IN ANALYSIS OF FIELD SAMPLES

| Analysis | Method Ref. | Description |
|---|---|---|
| Alkalinity | EPA 310.1 | Manual Titration |
| Chloride | EPA 325.2 | Automated Ferricyanide |
| pH | EPA 150.1 | Electrode |
| Sulfate | EPA 375.2 | Methylthymol Blue |
| Total Selenium | EPA 270.2 | Graphite Furnace AAS |
| Selenium Species | — | Ion Chromatography |

## TABLE 7. ANALYTICAL RESULTS FOR FIELD SAMPLES

| Sample Name | Total Selenium (ug/l) | Sulfate (mg/l) | Choride (mg/l) | Alkalinity (mg/l $CaCO_3$) | pH (Units) | Se(VI) (ug/l) | Se(IV) (ug/l) |
|---|---|---|---|---|---|---|---|
| A(KS) | 150 | 440 | 19 | 270 | 7.7 | 35 | 106 |
| B(KS) | 80 | 200 | 37 | 230 | 7.9 | 44 | ND |
| C(KS) | 30 | 129 | 57 | 270 | 7.7 | ND | ND |
| D(KS) | 60 | 320 | 119 | 320 | 7.3 | ND | ND |
| E(KS) | 10 | 133 | 25 | 40 | 7.4 | NA | NA |
| F(KS) | <1 | 172 | 482 | 240 | 7.9 | NA | NA |
| G(KS) | 16 | 480 | 18 | 300 | 7.6 | ND | ND |
| H(KS) | 12 | 79 | 28 | 290 | 7.8 | NA | NA |
| I(CO) | 620 | 990 | 191 | 290 | 7.6 | 342 | ND |
| J(CO) | 60 | 485 | 110 | 310 | 7.4 | NA | NA |
| K(CO) | 19 | 168 | 49 | 320 | 7.9 | NA | NA |
| L(CO) | 10 | 166 | 61 | 165 | ** | NA | NA |
| M(CO) | 17 | 173 | 58 | 280 | 7.8 | NA | NA |
| N(CO) | 10 | 178 | 46 | 220 | 7.9 | NA | NA |
| O(CO | 15 | 162 | 65 | 220 | 7.7 | NA | NA |
| P(OK) | 10 | 77 | 165 | 250 | 8.0 | NA | NA |
| Q(OK) | 17 | 53 | 5.9 | 320 | 8.8 | NA | NA |
| R(OK) | 8 | 81 | 95 | 340 | 7.6 | NA | NA |
| S(OK) | 70 | 145 | 160 | 380 | 7.7 | NA | NA |
| T(SD) | 19 | 177 | 11 | 320 | 7.9 | NA | NA |
| U(SD*) | 30 | 870 | 254 | 210 | 7.7 | NA | NA |

*Traces of chlorine in raw sample.
**Insufficient sample for analysis.
ND = Not Detected
NA = Not Analyzed

KS = Kansas
CO = Colorado
OK = Oklahoma
SD = South Dakota

Of the 3 samples for which selenate and selenite values could be obtained, the distribution of species was approximately 50% selenite, 50% selenate for 2 of the samples and approximately 70% selenite, 30% selenate for the third. Comparison of the total selenium and sulfate concentrations for the samples does not reveal any particular relationship other than the fact that the sulfate concentration is approximately 3 orders of magnitude higher than the selenate concentration.

The preservation study performed on the mixed 25 ppb selenite-selenate standards prior to collection of the field samples had indicated stability for both species for at least 3 weeks. Two of the field samples (A(KS) and S(CO)) were reanalyzed by AAS after their holding time exceeded 4 weeks and significant deterioration of the total selenium concentration was found.

For the case of A(KS) the AAS rerun was performed on the 2 month old unpreserved sample because the preserved aliquot had been discarded. The total selenium concentration had decreased to approximately half its original value, from 150 ug/l to 74 ug/l. IC analysis revealed that the selenate concentration had increased 40% (from 35 ug/l to 49 ug/l) while the selenite concentration had decreased from 106 ppb to 32 ppb. Selenite is known to be much less soluble than selenate and the data indicates that selenite may have precipitated from solution. As in the original analysis of the sample when it was 4 weeks old, agreement between the total selenium value by AAS and the sum of the species by IC is excellent (74 ug/l vs. 81 ug/l).

To determine the temporal stability of the acid preserved aliquots, the S(CO) sample which had an initial total selenium value of 60 ug/l was reanalyzed by AAS on both the preserved and unpreserved aliquots when the sample was 2 months old. This was one of the samples which was not analyzed by IC because it exceeded the 4 week holding time before it could be analyzed. The values in both aliquots had decreased to 17 ug/l, indicating poor stability even in acid preserved samples.

These results seem to indicate that analysis of samples held over 4 weeks is questionable even when acid preserved and the concentration decrease might be due to a combination of selenite conversion to selenate and loss of selenite from solution due to adsorption on container walls or precipitation. Sufficient data is lacking however, to rigoriously support this hypothesis. This might also provide an alternative explanation of why neither selenite or selenate was observed in the (CKS), D(KS) samples. Both samples were 2 months old when analyzed by ion chromatography and so their initial selenium concentrations of 30 and 60 ug/l determined by AAS before the sample had been held for 4 weeks might have significantly deteriorated.

## SECTION 10

## FUTURE CONSIDERATIONS AND ALTERNATIVES

The results of the field sample analyses reveal that ion chromatography with conductivity detection is not sensitive enough to detect selenium species at the levels found in many ground waters due to the sulfate, chloride, and nitrate interferences and because the instrumental detection limit for each speices is only marginally adequate. There are four analytical modifications which might improve the detection limit so that the low levels of selenium observed in the field samples could be speciated. These modifications are:

a. Use of off-line loading of a concentrator column prior to analysis by IC.

b. Use of IC to achieve separation of species and subsequent detection by graphite furnace AAS.

c. Use of recycle chromatography.

d. Use of UV detection instead of conductivity detection IC.

e. Analysis of field samples with higher levels of selenium.

a. Off-Line Loading of a Concentrator Column

This is a method for improving the instrumental detection limit of IC by concentrating a known sample volume on a precolumn prior to analysis. The anions are retained on the column while the rest of the sample passes through. The drawback is that the column will concentrate the interfering anions as well as the selenite and selenate. Improved instrumental detection limit is obtained at the price of greater interferences. Since the sulfate interference was successfully removed with $Ba(OH)_2$ addition for samples analyzed without preconcentration, it should work here provided that the increase in the sulfate concentration is calculated and the appropriate dose of barium is added. If this method does provide an adquate detection limit for selenate, the selenite value could be obtained as the difference between the selenate concentration and total selenium concentration determined by AAS. The off-column loading procedure is a manual, time-consuming process not well suited for routine analysis. If column loading gives an adequate detection limit for selenate, loading could be automated by reconfiguring the instrument and installing an additional pump.

b. IC Separation Coupled with AAS Detection

This procedure uses the ion chromatograph to separate the selenite and selenate species, but uses a graphite furnace AAS for detection rather than the less sensitive conductivity detector of the IC. The passage time of the selenite and selenate species through the ion chromatograph must be timed and the appropriate fractions collected from the waste line for analysis by AAS. Graphite furnace AAS has an instrumental detection limit of 1 ppb and does not suffer from the sulfate and chloride interferene problems found in IC. The drawback to this procedure is that the selenium concentrations in the collected fractions will be diluted from their initial sample concentrations because of the eluent fraction which must be collected along with the selenium species. It is therfore not clear how much of an improvement in detection limit for selenite or selenate this procedure offers. Assuming an eluent flow rate of 2 ml/min and a collection interval of one minute around the species retention time, the species will go from an initial sample

volume of 600 ul to an eluent volume of 2 ml. Therefore the improvements in detection limit by switching to AA detection (8 ppb vs. 1 ppb) will be offset by approximately a three-fold dilution factor.

c. Recycle Ion Chromatography

Recycle ion chromatography has been investigated by EPA as a potential method for achieving resolution of a peak which is competely buried under a much higher concentration adjacent peak. The procedure consists of collecting the portion of eluent containing the species of interest on a concentration column and reinjecting the concentrated sample under the original chromatographic conditions. This method effectively combines the use of concentrator column loading suggested in (a) with IC separation of the selenate species as suggested n (b). Recenty published EPA results for recycle ion chromatography revaled a maximum reliably separated molar ratio of 1300 for sulfate/selenate.[14] The sulfate/total selenium ratios of the 21 field samples analyzed for this report were all well above this molar ratio indicating the need for further refinement or modification of this method.

d. UV Detection IC

The ion chromatograph may be equipped with several different detectors in place of the traditional conductivity detector. Substitution of a UV detector would eliminate most of the interference problems since sulfate and chloride are both nonabsorbant. Interference of nitrate with selenite would persist, since nitrate is UV absorbant. Although a UV detector would remove interferences, UV detection is much less sensitive for selenite and selenate than conditivity detection when utilizing standard instrumental conditions. One published source gives a detection limit of 500 ug/l for selenite and 15 mg/l for selenate using standard operating conditions and a 100 ul loop[15]. Experimental work is needed to discern whether UV detection could provide adequate detection limits if column concentration was employed or instrumental parameters were varied. Even if UV detection could only provide detection limits comparable to those achieved with conductivity detection, this method would still be perferable if it eliminated the sulfate and chloride interferences.

e. Analysis of Field Samples with Higher Levels of Selenium

Conductivity detection IC coupled with barium hydroxide sample pretreatment is probably adequate for analyzing ground water samples if the total selenium concentration is greater than 50 ppb. Selenite could then be obtained by difference. An exact matrix dependent detection limit for selenate is not known but lies somewhere between 15 and 25 ppb. Even with a matrix detection limit for selenate of 25 ppb it should be possible to determine the predominant selenium species in a ground water sample with a total selenium value greater than 50 ppb. If no selenate or selenite peak is detected, then the selenate value is below the matrix detection limit of 25 ppb and selenite is the predominant species.

The majority of field samples received for this study did not represent the high selenium concentration ground waters requiring removal treatment. A recent study[16] was performed in Jade Hills and Red Butte, Wyoming to assess the correlation between increased body burden of selenium and elevated selenium levels in drinking water. These communities had total selenium concentrations in their drinking water of 190 and 493 ppb respectively. It might be of value to analyze a set of ground water samples from

communities with known high levels of selenium, such as Red Butte, by barium pretreatment and conductivity detection IC. Utilizing current analytical methodology the predominant selenium species in these higher level field samples could definitely be determined. This would enable assessment of the feasibility of selenium removal by activitated aluminum for the types of waters which would actually require treatment.

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Date

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